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ONTARIO

MINISTRY OF THE ENVIRONMENT

WASTE CONTROL PROBLEMS

in the

MINING INDUSTRY

Technical Papers and Articles

published by the

ONTARIO WATER RESOURCES COMMISSION

Division of Industrial Wastes

1970 - 1971

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WASTE CONTROL PROBLEMS IN THE
MINING INDUSTRY

TECHNICAL PAPERS AND ARTICLES

published by

THE ONTARIO WATER RESOURCES COMMISSION
DIVISION OF INDUSTRIAL WASTES

1970 - 1971

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ASPECTS OF WASTE CONTROL IN THE
MINING INDUSTRY

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A paper presented at the thirteenth Conference on
Great Lakes Research, April 2, 1970, Buffalo, N.Y.

INTRODUCTION

The mining industry in Ontario had a very humble beginning in the early 1800's with the development of a small iron ore plant. This was followed by major discoveries of nickel and copper in 1883, silver in 1903, gold in 1908, iron in 1939, uranium in 1953 and lead and zinc in 1967. During the past two years (1968 and 1969) the annual mineral wealth mined in the Province of Ontario exceeded one billion dollars which represented about one-quarter of Canada's total output. In mining, Canada leads the world in the production of asbestos, nickel, zinc, nephtheline syenite, silver and selenium and ranks second in the world of the production of gold, lead, molybdenum, platinum, potash, sulphur, aluminum, titanium ore and uranium.

Unfortunately, the exploitation of our mineral resources has not occurred without some expense being incurred on another natural resource - our waters. The purpose of this paper is to outline the origin and nature of wastes arising out of mining operations, to define the status of waste control in the mining industry and to describe some of the specific steps being taken by some mining companies towards pollution control.

In this paper, the aspects of waste control to be dealt with will be:

- (i) Tailings Disposal and Containment
- (ii) Mine Water Disposal

(iii) Tailings Overflows

(iv) Acid Mine Drainage

(i) Tailings Disposal and Containment

Solids waste disposal is the principal problem in the mining industry. In the mining industry, these waste solids are called mill tailings and constitute the waste materials after the minerals have been extracted from the ore. When one considers that the mineral values can range from as low as less than 0.1 percent up to greater than 10 percent, it can be appreciated that the provision for proper mill tailings disposal is a consideration of prime importance. Based on the available production figures, it is estimated that in Ontario alone, some 80 million tons of waste mill tailings must be disposed of annually. This amount of tailings would occupy an area of 1000 acres to a depth of almost 30 feet.

Waste mill tailings have been disposed of in lakes, low-lying swampy areas, natural depressions near the mines, enclosed valleys and in engineered impoundment basins. Properly designed for each particular situation, the latter point of disposal provides the best long term disposal of waste mill tailings.

Because of the indiscriminate discharge of waste mill tailings by some mining companies in the past, some tailings disposal areas present not only a potential hazard to the environment due to the possibility of a massive discharge of the tailings to a watercourse but also a continuing source of pollution to the

environment in the form of:

- a) Water pollution - arising from the leaching of soluble matter in the tailings into a watercourse; erosion occurring on the dam slope as a result of seepage.
- b) Air Pollution - wind blowing of fine dust from abandoned areas; a potential water pollution problem from the wind blown dust also exists.
- c) Aesthetic Pollution - the sterile waste piles do nothing to enhance the landscape of the surrounding area.

All of the foregoing are present in varying degrees at most mining operations.

It has generally been the practice of mining companies to dispose of waste mill tailings by the cheapest and most convenient method possible. Impoundment basins and dams for the containment of tailings in valleys were constructed principally by practical time proven methods as opposed to sound engineering principles. Little, if any, thought was given to planning with respect to ensuring that the tailings area posed no threat to the environment both during and upon cessation of mining operations. To-day with the increased awareness on part of the public who are demanding more exacting controls in all areas of pollution control and further, with the greater pressures being applied by the reg-

ulatory agencies, most mining companies are now giving greater attention to the location and design of tailings disposal areas.

There are many factors which must be considered in the design of dams for the empoundment of waste mill tailings. Without going into detailed soil mechanics, some of these factors are; presence of watercourses in the proposed area, stability of foundation material, material available for dam construction, top width of dam, amount of freeboard to be maintained in the tailings area, provision for seepage control and protection for erosion control on the outer bank. Proper consideration of these factors for each situation will go a long way towards ensuring the stability of the dam structure. Under no circumstances should the requirements be relaxed because a particular mine is located in a remote area where a potential dam failure will not have any great effects. It is the obligation of every mining company regardless of its location, to adhere sound engineering principles in the design of impoundment basins for their wastes.

Once placed into use, it goes without saying that proper supervision and maintenance of the tailings area is required to ensure continued stability, but there are also some operating practices which further increase the integrity of the dam structure. The main point which deserves comment here is the method whereby tailings are introduced into the impoundment area. It is still common practice at many mines to use a single point of entry for

the wastes. This practice results in high and low ends in the dam with the consequent tendency for the pond to be forced to the lower end. The result is that the lower end of the dam becomes built up with the fine material of the tailings and thereby increases the possibility of seepage erosion and shear failures of the outer dam face in this area. To overcome the disadvantage of the single point entry, the preferred method is to have the tailings pipeline located around the periphery of the tailings dam to permit a dribble system to be established at intervals along the pipeline. In the mining industry, this practice is commonly known as "spigotting." This form of feeding ensures that a beach of even width containing the coarser sands will be formed adjacent to the dam wall and results in the finer materials being directed towards the centre of the area. The coarse sands can be readily used to raise the dam wall as required.

While the proper design and operation of the tailings disposal area is of primary concern, there is also a need on the part of mining companies to undertake steps to control wind and water erosion of the banks of the tailings dam as well as planning for long-term controls that will aid in possible future contamination of the environment. Windbreaks in the form of a snowfence or by planting rows of fast growing poplar or willow trees are often used to contain the tailings within the area. Other methods tried to protect the banks include the covering of the slopes with waste rock, slag and a straw mulch. These methods have

met with only limited success and it appears that vegetation is the best practical answer for the stabilization of tailings banks and abandoned tailings areas.

The establishment of a permanent cover of vegetation involves not merely growing plants, but necessitates bringing into being a plant community that will maintain itself indefinitely without further attention or artificial aid such as irrigation. Such permanence is only achieved by selecting species of plants or grasses that will grow, spread and reproduce under the poor soil conditions encountered with tailings areas. A number of abandoned tailings areas in Ontario have been successfully rehabilitated by the promotion of vegetation, these being by the International Nickel Company of Canada in Sudbury and by the gold mines in the Timmins area.

(ii) Mine Water Disposal

Mine water results from the underground operations on a mining property. The water which may be initially present due to an underground source in the orebody or may be pumped down from the surface is used principally for dust control and drill cooling and becomes contaminated with suspended matter. Mine water through its intimate contact with the orebody may also contain heavy metals and other toxic materials in sufficient concentrations to render it undesirable for direct discharge

to the watercourse. The nature of the orebody, such as the presence of sulphides, can cause acidic conditions in the mine water.

Over the years, most mining companies discharged this mine water directly to the watercourse or into the tailings area. Only in recent years has it been realized that the small amount of mineral values contained in the mine water could be recovered through its use in the milling circuits. For example, in the uranium industry the mine water is used in the grinding circuit and wherever else it is technically practicable as it does contain considerable uranium values. One mine in the Elliot Lake area which is being kept dewatered in anticipation of the resumption of operations treats mine water exclusively. Another mine in the same area for many years now has promoted bacterial leaching of the uranium from the mine stopes under controlled conditions recovering the uranium from the mine water by means of ion exchange.

Where the only problem of mine water is associated with the presence of suspended matter, the simplest solution is the use of this mine water to slurry the mill tailing so that they can be pumped to the tailings area. If this is not feasible, the mine water is pumped directly to the tailings area. However, not all mines are located adjacent to the mill such as is the

case in the Sudbury area. Under such circumstances, it becomes necessary to construct clarification facilities for solids removal to render the mine water satisfactory for discharge directly to the watercourse. Often, these clarification systems are located underground at some point where all the mine water can be centrally collected and then the clarified water is pumped to the surface.

(iii) Tailings Overflows

Tailings overflows or decants are those liquid wastes which are discharged directly to the watercourse from the tailings area. In a properly constructed tailings area equipped with a well-designed decant structure, this tailings overflow is generally satisfactory for discharge directly to a watercourse from the standpoint of its suspended solids content. However, the dissolved solids concentration and chemistry can vary considerably with each mining operation depending on such factors as the mineral mined, the orebody, the mill process, the chemicals used, etc. By categorizing the mining industry, it is nevertheless, possible to discuss some of the problems which are common to a specific segment of the industry. It is not possible to attain complete recovery of the mineral from the ore and that which remains is discharged with the waste tailings. These minerals are most often in the insoluble state but a small fraction does get dissolved and in the case of base metal mining operations,

(copper, lead, zinc and nickel) the concentrations of these metals often exceed the objectives for direct discharge to a watercourse. The solution to this problem is very difficult since the concentrations are normally in the 1 - 5 parts per million range. The most practical approach would be to reuse the tailings overflow in the milling circuits thereby eliminating the discharge completely. An example of where this is done is at the International Nickel Company of Canada in Sudbury which reuses 100 million gallons of water per day out of its total requirement of 133 million gallons per day. In addition to tailings overflows INCO also reuses mine wastewater and sewage treatment plant effluents.

In precious metal mining (gold and silver) problems in tailings overflows arise out of the presence of toxic compounds - namely cyanide and arsenic. Cyanide is present in effluents from gold mining operations where it is used to extract the gold from the ore. On the other hand, arsenic is commonly found in association with silver-bearing ores. Natural oxidation in the tailings area will reduce the cyanide levels somewhat before the effluent reaches the watercourse but often the levels still exceed the desired objectives. Treatment of the tailings overflow for cyanide removal does not appear practical and the key to the elimination of this problem lies in better control of the mill process to provide complete cyanide utilization in the mill circuits. The arsenic problem in silver

mining can be overcome by the addition of sufficient lime to the tailings as they are discharged to the tailings area. The resultant arsenic salt formed is virtually insoluble.

In the uranium mining industry, the problem lies in the presence of radioactive compound. Of primary concern to date has been the presence of radium-226 but there are other radioactive compounds such as thorium-232 and lead-210 which may be present in undesirable concentrations. Radium-226 is naturally present in very small quantities in all uranium-bearing ores. Most of the radium remains in the undissolved state throughout the mining and milling operations but a very small amount (about 1 percent) does dissolve and finds its way into the tailings effluent. Even this small amount results in concentrations which exceed the desired water quality objective of 3 picocuries per litre. In the uranium mining industry, it has been necessary to provide treatment of the tailings overflow to effect radium removal. This has been achieved by means of the addition of barium chloride which reacts with the radium and the sulphates in the tailings overflow to form a barium sulphate-radium precipitate which is allowed to settle in a subsequent impoundment area before the overflow is discharged to the watercourse. This treatment used by Denison Mines Limited and Rio Algom Mines provides greater than 90 percent radium removal.

The processing of ore to recover the particular metal involved requires the extensive use of chemical reagents.

For example, 72 pounds of sulphuric acid, 42 pounds of calcium oxide, 2 pounds of nitric acid, 0.4 pounds of ammonia and small amounts of glue and flocculant are required to process one ton of uranium ore. Most of these chemicals along with other materials dissolved from the ore but not recovered end up in the tailings overflow. Some of the undesirable contaminants encountered in tailings overflows are acidity, alkalinity, nitrates sulphates, hardness and iron. Because of the large volumes of tailings overflow involved, the treatment for removal of these dissolved contaminants is both impractical and uneconomical. The most practical solution lies in the reuse of the tailings overflow in the mining and milling operations.

(iv) Acid Mine Drainage

Most of the important metals, such as copper, nickel, lead and zinc, that are presently being mined in Ontario occur in the ore as sulphides. In addition, the orebodies of uranium, the precious metals and in some cases iron, are characterized by large quantities of "gangue" sulphides (principally FeS_2 - pyrite and Fe_7S_8 pyrrhotite.) At present, many mining operations in the province include mills that reject these gangue sulphides. These gangue sulphides usually end up in the tailings area and sooner or later react to form materials that migrate into adjacent watercourses. The result is acid mine drainage. Because there are generally no facilities to treat the tailings

overflow, chemical reactions occur downstream that result in a gradual but further deterioration of stream water quality.

Sulphide ores are relatively stable in their natural environment and it is only when the environmental conditions change that marked chemical changes result. In mining, these changes occur quite rapidly when the sulphide ore is broken down thus resulting in depressed pH conditions in the waste. The low pH also influences the dissolved solids content of the waste by creating conditions whereby greater dissolution of sulphates and heavy metals occurs.

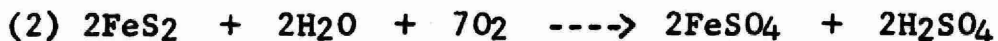
The mechanism of acid production of sulphide-bearing ores has been widely researched and it is generally agreed that nearly all of the naturally occurring sulphides react in a similar manner when exposed to a moist oxygen containing atmosphere. The following equations, based on the alteration of pyrite, a very common sulphide, can be considered as representative:

Step I - Sulphide to Sulphate

When natural sulphuritic material in the form of sulphide and usually in combination with iron is exposed to the atmosphere (oxygen) it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition. In the first circumstance, assuming the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of ferrous sulphate.



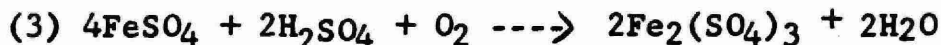
If, however, the oxidative procedure proceeds in the presence of a sufficient quantity of water (or water vapour) then the direct formation of sulphuric acid as well as ferrous sulphate in equal parts will result.



It should be noted that in the majority of mine environments, it is believed that the latter reaction occurs.

Step II Oxidation of Iron (Ferrous to Ferric)

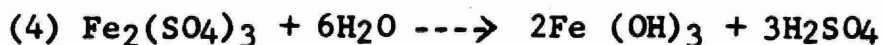
Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state with the formation of ferric sulphate.



Water is not limiting for this reaction since it is not a requirement but rather a product of the reaction.

Step III - Precipitation of Iron

The ferric iron associated with the sulphate then combines with the hydroxyl ion of the water to form ferric hydroxide. In an acid environment, ferric hydroxide is relatively insoluble and precipitates.



It should also be noted that another possible reaction has been suggested in the case of ferric sulphate. The ferric ion may enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion causes the oxidation of further amounts of sulphuritic materials to the sulphate form, thereby

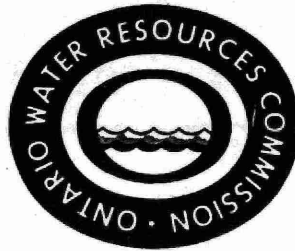
accelerating the acid formation process.

The present methods of control of acid mine drainage are clearly not adequate. At large mining operations such as in the Sudbury area it is economical to utilize the sulphides to produce sulphuric acid. At smaller operations, it becomes necessary to provide some type of treatment. Lime addition at the mills prior to discharge to the tailings area is generally not satisfactory in correcting the downstream acidity problem. The solution therefore would appear to lie in the treatment of tailings overflow. In such cases, downstream retention areas for settlement of the precipitate are required. Perhaps, the most practical solution in overcoming this problem lies in the segregation of the sulphide wastes from the other mill tailings for disposal in a separate impoundment area where treatment becomes more manageable.

SUMMARY

In summary, the mining industry is faced with many problems, not the least of which is water pollution, in the extraction of the metal from the ore. Because of the remoteness of most mining operations, less than adequate measures were taken by mining companies towards the conservation of the environment. However, with the increased awareness on the part of the public who are demanding a cleaner environment, with the increased surveillance on the part of the regulatory agencies on all aspects of the mining industry and with the realization by the industry that the development of one natural resource cannot be undertaken at

the expense of another valuable resource, it is expected that many of the problems presently being encountered in the mining industry will be successfully overcome.



THE PROBLEM OF ACID MINE DRAINAGE
IN ONTARIO

by

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A paper presented at the Third Annual Meeting
of the Canadian Mineral Processors
January 12, 20 and 21, 1971.

OTTAWA, Canada.

THE PROBLEM OF ACID MINE DRAINAGE IN ONTARIO

Even though acid mine drainage is an old problem, particularly in coal mining areas, its appearance in the form of a major environmental hazard in the hardrock mining districts of Ontario was unexpected. The yellow and amber coloured wastes that characterize an acid mine drainage situation were first noted by the Ontario Water Resources Commission in the uranium mining Elliot Lake district. Problems of a similar nature were also noted in the copper-lead-zinc camp at Manitouwadge, the nickel camp at Sudbury and at numerous isolated base metal properties, both in and out of the Province of Ontario.

Without exception, when acid mine drainage type effluents were evident, the specific companies involved worked sulphide or sulphide-associated ores. Without exception, the ore bodies contained quantities of iron sulphide (in various mineralogical forms) and, without exception, the milling circuits serving these operations were such that the iron sulphides were rejected to the tailings areas as waste.

Once in a tailings area and after a varying period of time, iron sulphides react to form water soluble salts which, when discharged in the effluents from the tailings area, can affect stream chemistry and stream ecology.

It is not unusual that the minerals pyrite, marcasite and pyrrhotite (all iron sulphides) react to form a stable oxide under atmospheric conditions. The law of stability of rocks and minerals, for instance, states that rocks and minerals are stable only in the environment of their formation and, as the environment surrounding them changes, the rocks and minerals tend to change to other species which are relatively more nearly stable under the conditions of the new environment (a). Under atmospheric conditions, iron oxide exhibits a greater stability than iron sulphide.

The basic reactions that describe the chemistry of an acid mine drainage situation are well known and are detailed here as a simple review (b):

Reaction #1 (Sulphide to Sulphate)

When natural sulphuritic material in the form of a

sulphide (and usually in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition:

- (a) Assuming that the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:



- (b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:



In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 [Oxidation of Iron (Ferrous to Ferric)]

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:



Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (*T. ferrooxidans*) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 (Precipitation of Iron)

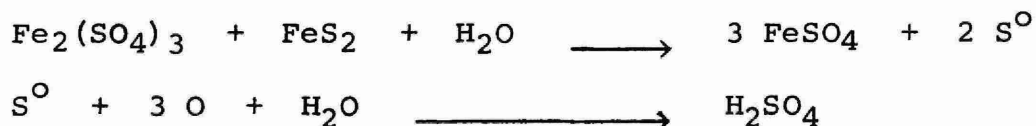
The ferric iron associated with the sulphate ion commonly combines with the hydroxyl (OH^-) ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric

hydroxide is largely insoluble and accordingly precipitates:



IMPORTANT NOTE:

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:



The fact that very little 'free' sulphuric acid is found in mine waste drainage is probably due to the reactions between other soluble mineral species and sulphuric acid.

The iron sulphides, of course, are not the only sulphides that find their way into the tailings areas. Mill recoveries are seldom greater than 97 percent and, as such, limited quantities of ore materials also become an integral part of the tailings mass. The ore materials are generally sulphides themselves (chalcopyrite, galena, sphalerite, etc.) and, therefore, enter into oxidation reactions that, in a simple sense, tend to resemble the iron sulphide oxidation reactions that have already been described.

When the correct conditions are presented, sulphide minerals in a tailings mass will oxidize to the corresponding metal ions plus the sulphate ion. Generally speaking, the sulphate ion will leave the tailings area. The metal ions on the other hand, depending on many chemical factors, may be precipitated as 'insoluble' hydroxides, oxides, carbonates, sulphates or silicates, etc., and hence be retained within the tailings area or may be carried away in solution from the site of oxidation and hence leave the tailings area. Iron, copper,

cobalt, manganese, zinc and nickel all form soluble salts (usually sulphates) under acid mine drainage conditions and are, therefore, commonly detected in the effluents from affected areas. Lead, on the other hand, forms a relatively insoluble sulphate (known as the mineral anglesite in geology texts) and is therefore only rarely detected in concentrations greater than 1 part per million under similar circumstances.

The factors that govern the rate of the geochemical destruction of the naturally occurring inorganic sulphides are essentially the same factors that govern the rate of any chemical reaction that takes place. However, each factor must be modified or amplified to suit the processes of nature. The single most important factor is probably available surface area. If the total available surface area of any substance that is subject to a chemical reaction is increased, the rate of reaction itself increases. It then seems to follow that, if the total surface area of a sulphide mass is increased, the rate of the geochemical decomposition of that mass will also increase. As partial proof of this, consider sulphide orebodies which usually outcrop to a limited extent if at all. In many countries of the world, sulphide orebodies show signs of weathering to a depth of several hundred feet and indications of weathering to a depth of over one thousand feet have been recorded. This alteration at depth can only be explained by the apparent existence of secondary surfaces in the deposit. Secondary surfaces, commonly the result of unbalanced stresses and strains within a deposit are generally created mechanically and are given such names as faults, joints and torsion cracks, etc. As a result of faulting, etc, coupled on occasion with diverse solution effects, very sophisticated natural drainage networks can be set up within a particular deposit. The network can be so efficient, in fact, that a company working the deposit has to rely heavily on pumps to keep the workings dry. The water percolating through the deposit may bring oxygen, among other substances, into direct contact with the sulphide ore. The sulphide ore reacts to produce water soluble salts and sulphuric acid. The water that brought the oxygen to the ore also removes the soluble reaction products from the ore and thus permits the continuation of the reaction. When this solution gains access to mine workings, it is generally

characterized by a relatively low pH, a relatively high sulphate content and an abnormal concentration of the various heavy metals. In appearance, it may be clear and colourless or it may be coloured light-yellow, dark-yellow, amber or rusty orange. The various colours are due to the state of oxidation of the iron present. If, by chance, cemented backfill is used in the mine, the highly alkaline underflow from backfilled areas will perhaps mask (by neutralization) the original acid characteristics of the mine water but the acid situation within the deposit still exists nonetheless.

To relate this discussion to a tailings area is quite simple. A tailings area of the type we are discussing can be regarded as nothing more than a highly fractured sulphide 'ore body'. The enormous secondary surface area of the 'ore body' has been created mechanically as a result of crushing and grinding in the mill. Oxygen-carrying water has ultimate access to virtually every particle in the mass. It is only logical to suspect therefore that a tailings area that contains quantities of iron sulphide will (unless the gangue in the original ore has sufficient residual neutralizing capacity and this is generally not the case) produce phenomenal quantities of water-soluble acid-producing salts.

Tailings areas that are well known as acid producers within the Province of Ontario have been examined in detail. The iron sulphide content of these areas varies, so far, from a minimum of 2.5 percent to a maximum of 72 percent. Many other properties with sulphide contents within this range are known.

Iron sulphide occurs in three principal forms in the tailings areas of the Province:

- (i) pyrite
- (ii) marcasite
- (iii) pyrrhotite

Pyrite is an isometric form of ferrous disulphide. Marcasite is also ferrous disulphide but is orthorhombic in nature. Pyrrhotite is a hexagonal form of ferrous sulphide

that contains a slight excess of sulphur.

The rates of reaction of pyrite, marcasite and pyrrhotite under typical acid mine drainage circumstances are said to be significantly different. It has been reported (c), for instance, that marcasite reacts 9 times as fast as good quality pyrite. On the other hand, impure sulphide material (corresponding perhaps to poor quality pyrrhotite) is said to react up to 81 times as fast as good quality pyrite. These facts are interesting but they are really not too significant as far as the Ontario mining industry is concerned. Severe acid mine drainage problems are known to occur in Ontario where marcasite and pyrrhotite are, relatively speaking, absent. In addition, most of the tailings areas in Ontario of the type we are discussing contain intimate mixtures of two or more iron sulphide species.

If sufficient care is taken during the years of conventional mine-mill operations, the inherent alkalinity of most flotation circuits plus perhaps minor lime additions should control any tendency towards an acid mine drainage situation where the main decant is concerned. However, during the same period, that is, the operational life of the mine-mill complex, there is a very good chance that the underflow (seepage) from the tailings area will gradually become highly acid in nature and will therefore require extensive chemical treatment if environmental standards are to be maintained. In fact, in the Province of Ontario, it is primarily the untreated seepage discharges from active tailings areas plus uncontrolled runoff and seepage from abandoned areas that gives rise to the undesirable waste discharges that we refer to as acid mine drainage.

Acid mine drainage in Ontario is cumulative. Abandoned properties will continue to produce 'acid' for decades. As the number of abandoned sulphide operations increases, the acid load that our environment must assimilate also increases. Thus this is a problem of immediate concern which must be brought under effective control.

At the present time almost fifty square miles of the Province of Ontario are covered by active and abandoned tailings

areas. For the most part, these tailings areas occupy depressions that at one time were the site of lakes or very wet swamps. When a lake is inundated with tailings, it does not disappear. It merely exists as a 'ghost' within the tailings mass and occupies the spaces between tailings particles. The watershed that fed the 'former' lake does not disappear either. It now feeds the tailings area. If the lake overflowed continuously before tailings deposition, it will overflow after tailings deposition. Generally, however, the overflow will not be noticeable until the tailings area is completely abandoned. We then call the overflow 'seepage'.

True seepage, that is water that has percolated a considerable distance through sulphide bearing tails, is by nature highly contaminated. Consider the following seepage sample from an abandoned tailings area in the Elliot Lake district:

pH	2.0
Sulphate as $\text{SO}_4^{=}$	7,440 ppm
Acidity as CaCO_3	14,600 ppm
Ferric Iron as Fe	1,450 ppm
Ferrous Iron as Fe	1,750 ppm
Uranium as U	7.2 ppm
Zinc as Zn	11.4 ppm
Nickel as Ni	3.2 ppm
Cobalt as Co	3.8 ppm
Copper as Cu	3.6 ppm
Manganese as Mn	5.6 ppm
Aluminum as Al	588 ppm
Lead as Pb	0.67 ppm
Cadmium as Cd	0.05 ppm
Lithium as Li	0.07 ppm
Vanadium as V	20 ppm
Silver as Ag	0.05 ppm
Titanium as Ti	15 ppm
Magnesium as Mg	106 ppm
Calcium as Ca	416 ppm
Potassium as K	69.5 ppm
Sodium as Na	920 ppm
Arsenic as As	0.74 ppm
Phosphorus as P	5.0 ppm
Chemical Oxygen Demand	270 ppm

The above sample, when taken, was clear, colourless and sparkling in appearance.

One characteristic of true seepage flows is their inherent abnormal heavy metals content. The metals present and their relative concentrations vary from property to property. Metals in solution are always present and, therefore, in order to preserve our aquatic environment, the removal of these substances must form an integral part of any treatment process that is to be applied to this type of effluent or, indeed, to any of the effluents that arise from mining, milling and tailings disposal operations.

How do trace elements affect the stream ecology(d)? Toxic metals act in several ways. Salts of electropositive metals such as silver, molybdenum, antimony, thallium and tungsten react with proteins and destroy metabolites essential to vital function. Some metals pervade the active sites of an enzyme and render it useless through substitution for the normal metal constituents. These metals are selenium and tellurium and, to a much lesser extent, beryllium. Precipitation and chelation of essential metabolites is the mode of toxic action shown by aluminum, beryllium, scandium, titanium, yttrium, zirconium, barium and iron. Catalytic decomposition of proteins is shown by lanthanum and other rare earths. A final mode of toxic action is reaction with the cell membrane to alter its transport properties. Salts of gold, cadmium, copper, lead and uranium show this action.

It is clear that the problem of acid mine drainage in the Province of Ontario must be eliminated or at least minimized in the very near future. How can this be accomplished?

When involved in an acid mine drainage situation, we propose ten basic rules that can be and should be considered:

Rule #1

Define the Problem.

The average mine manager in today's world is expected

to be more than just a successful blend of engineer, geologist, metallurgist, chemist, physicist and economist. Now he is expected to be an ecologist.

On one hand the mine manager is harassed by the head office for spending too much on waste treatment; on the other hand, by the regulatory agencies for spending too little. At any rate, a mine manager can remove some of his worries concerning effluent treatment by simply knowing exactly what he is up against. He should have in his possession, for instance, a very detailed map of the property that he is responsible for. The map should indicate the source, direction and volume of all flows that enter and/or leave the property. Seepage flows from the tailings area should be accurately traced. A routine chemical analysis of each flow should be available. More important, a complete SCAN type analysis should be run at least once on all major flows from the property (a SCAN analysis is an analysis in which the chemist has attempted to identify and determine the amount of every contaminant in the flow).

When dealing with an acid mine drainage situation any analytical results should include pH, sulphates, acidity, iron, copper, zinc, cobalt, nickel, manganese and lead. In addition to the above, any SCAN type analysis should include the following:

vanadium
cadmium
mercury
tin
titanium
chromium
molybdenum
barium
lithium
sodium
potassium
calcium
aluminum
arsenic
phosphorus

If any heavy metal exists in the effluent or effluents from the property in concentrations greater than 1.0 part per million, it should be regarded as a potential source of trouble. It may cause downstream environmental problems. If, on the other hand, several heavy metals (e.g. cobalt, copper, zinc and nickel) occur in the effluent or effluents in concentrations of less than 1.0 part per million but the combined total is greater than 1.0 part per million, the synergistic effect (one ion acting with another) may be (and probably is) great enough to warrant concern.

Rule #2

Do not ignore the preliminary signs of an acid mine drainage situation.

Acid mine drainage symptoms develop long before acid mine drainage becomes the dominant chemical force in the tailings area. These symptoms are best observed in relatively small non-fluctuating seepage flows that emerge from the base of tailings dams on a property.

First the sulphate concentration begins a lazy climb upwards. This can generally be detected by periodic sampling of the same flow over a number of months. The tailings area decant should not be chosen for this type of work since sulphate additions in the mill, which tend to increase as production increases, make the establishment of a base sulphate concentration quite difficult. Also, the decant is fed by wastes that originate in the mill, run across the top of the tailings mass and then leave the area. Seepage, on the other hand, is a result of water percolating through a tailings mass and is therefore in a better position to pick up soluble oxidation products.

Since the sulphate concentration of most natural lakes, rivers and streams in northern Ontario is approximately 10 parts per million a reading of a few hundred parts per million sulphate in a seepage flow is cause for concern. Readings of 1,000 parts per million sulphate are very common when acid mine drainage conditions are well established.

Seepage flows containing in excess of 11,000 parts per million sulphate have been noted in the Elliot Lake district.

An increase in sulphate content usually coincides with a decrease in pH and an increase in the concentration of iron and other heavy metals.

When the pH drops to approximately 3.0, the situation becomes critical for reasons discussed later in this paper. Once the pH of the affected portions of the tailings mass drops below 3.0, the situation is practically irreversible and treatment costs become enormous.

Rule #3

Collect all effluents from a specific property at a common point for treatment before discharge to a watercourse.

Quite commonly, an acid mine drainage problem at a specific property is magnified in the eyes of the public by the simple fact that wastes are discharged not to one watercourse but to several. Most operations, of course, utilize one or more decant structures that discharge to a common depression, stream, or lake. However, what has been forgotten is that seepage flows which are generally low-volume highly-contaminated untreated flows, discharge from the base of almost every dam on the property. One or more of these flows will probably discharge into a stream or lake that is not related to the watercourse receiving the decant overflow. The result is the potential for impairment of two or more watercourses instead of one. Furthermore, two treatment systems would be required instead of one.

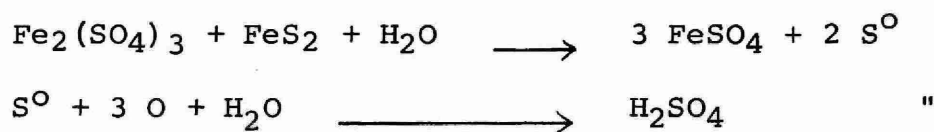
Rule #4

Do not mishandle raw seepage flows.

Raw (untreated) seepage flows usually contain excessive quantities of both ferrous and ferric sulphate - especially when the pH drops below 3.0 (a common occurrence). Reaction #3 in the iron sulphide oxidation sequence given previously in

this paper states:

"The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion 'backtriggers' the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:



Therefore, under no circumstances, should untreated seepage be collected and pumped back onto a tailings area. This is as close to 'acid mine drainage suicide' as a mine manager can possibly get. On the other hand, raw seepage can be collected and treated (neutralized) with lime (to a pH of 8.5) and then returned to the tailings area. This practice is acceptable but is still not advisable. Seepage flows are maintained, in part, by water ponding on the tailings area. Thus, by returning seepage, treated or untreated, to the tailings area the problem is aggravated.

Rule #5

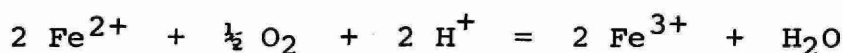
Use the forces of nature for acid mine drainage treatment whenever and wherever possible.

Characteristically, seepage flows that originate within a sulphidic tailings mass tend to change colour on standing while exposed to the atmosphere. Initially clear and colourless the waste assumes a faint yellow flush which, in time, gradually deepens to an intense amber-red. This latter colour is due to very finely divided suspended particles of hydrous ferric oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$).

Ferrous iron is quite commonly found as a component of acid seepage flows and, in Ontario, occasionally represents over 50 percent of the iron species present. If a flow contains a relatively high ferrous to ferric ratio, we term the flow

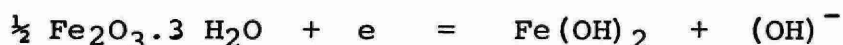
'immature'. If the ferrous to ferric ratio is low, the flow is termed 'mature'. Obviously, as the ferrous iron in any flow oxidizes, the ferrous to ferric ratio decreases and the flow itself matures. Thus, highly coloured flows tend to be mature flows; colourless flows tend to be immature flows.

Fortunately (e) the potential of the $\text{Fe}^{3+} - \text{Fe}^{2+}$ (ferric-ferrous) couple, 0.771 volts, is such that molecular oxygen can convert ferrous iron to ferric iron in acid solutions.



$$E^0 = 0.46 \text{ volts}$$

In a basic solution, of course, the oxidation process is still more favourable:



$$E^0 = -0.56 \text{ volts}$$

Neutral and acid solutions of ferrous iron oxidize less rapidly with increasing acidity (despite the fact that the potential of the oxidation reaction will become more positive).

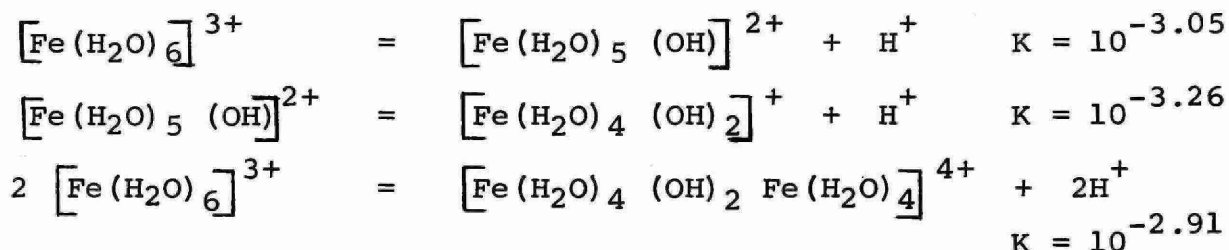
The oxidation of ferrous to ferric species by molecular oxygen appears to involve the initial formation of an ion FeO_2^{2+} . The reaction kinetics also suggest that a binuclear species is a transient intermediate formed by the attack of Fe^{2+} on FeO_2^{2+} . The overall reaction of



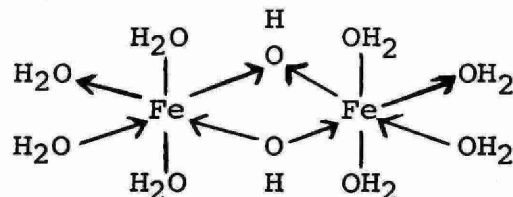
leads to the hydroperoxo ion which rapidly decomposes to give Fe^{3+} and HO_2^- , which itself either oxidizes Fe^{2+} or decomposes to O_2 .

One of the most conspicuous features of ferric iron (which all seepage flows of the type we are discussing contain) in aqueous solution is its tendency towards hydrolysis and/or formation of complexes. It has been established that the

hydrolysis is governed in its initial stages by the following equilibria constants:



In the last of the above equations, the binuclear species is written to imply the structure



which, though plausible, is quite unproved.

From the constants for these equilibria, it can be seen that even at the rather acid pH's of 2-3 (most acid seepage flows fall within or close to this range) the extent of hydrolysis is very great and, in fact, in order to have solutions containing ferric ion mainly (say approximately 99 percent) in the form of the pale purple hexaquo ion, the pH must be around zero. As the pH is raised above 2-3, more highly condensed species than the binuclear one noted above are formed. Attainment of equilibrium becomes sluggish and colloidal gels are formed. Ultimately, hydrous ferric oxide is precipitated. There is no evidence to suggest that any definite hydroxide, $\text{Fe}(\text{OH})_3$ exists and the reddish-brown precipitate commonly called ferric hydroxide is best described as hydrous ferric oxide, $\text{Fe}_2\text{O}_3 \cdot n \text{H}_2\text{O}$.

The various hydroxo species, such as $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ are yellow in colour because of charge transfer bands in the ultraviolet which have tails coming into the visible. Thus aqueous solutions of ferric salts even with non-complexing

anions are yellow unless extremely acid. As colloidal hydrous ferric oxide accumulates the colour of the 'solution' will change to amber-brown and, under unusual circumstances, to deep blood-red.

The fact that seepage waste does generally turn colour on standing and the fact that advanced inorganic chemistry texts indicate that favourable reactions can occur spontaneously led us to believe that one method of partially treating seepage waste involving essentially no reagent costs would be the simple ponding of such wastes. After two and one-half years study in the Elliot Lake district, we have concluded that such a method of pretreatment is both feasible and practical.

The cost of lime that is required to effectively neutralize (to a pH of 8.5) most seepage flows is prohibitive. Most of the lime (or NaOH, etc.) in this type of reaction is consumed not in reactions with free acid but in reactions with soluble (metal) salts (see Figure 3). This is all very well as the metals have to be removed in order that water quality standards can be met. However, any free acid that remains after metal precipitation still must be neutralized. The presence of a little free acid can cause a tremendous pH depression.

Natural ponding, inefficient as it may be, under the proper conditions will result in up to 50 percent reductions in metal and sulphate concentrations (effluent as opposed to influent). This, of course, represents a significant saving in neutralizing reagent costs.

Efficient ponding can be accomplished if the following conditions are satisfied:

- (a) The retention time (the time the waste is held in the pond) must be as great as possible (in the order of months rather than days).
- (b) The pond should be as shallow as possible (to enhance oxygen transfer from the atmosphere).
- (c) The pond waste should not be allowed to come into contact

with tailings containing iron sulphides (see Rule #4).

- (d) Wastes being decanted from the pond should be taken from the pond surface (preferably a sluice type overflow, etc.). The surface film of the pond is the zone of maximum oxidation and should therefore contain less unoxidized material than the waste a foot or so below the surface.

This type of seepage pretreatment facility can be set up in any swampy ravine or depression on the property. A crude low earth or log dam, a large beaver pond or a small stagnant pot-hole lake in the vicinity of the operation is all that is required. However, please note Rule #3. The overflow from this type of pretreatment facility should be directed to the area that receives the main decant overflow. In some cases, the residual alkalinity of the decant (providing, of course, that the decant itself is alkaline) may be all that is required for final seepage treatment.

The trace heavy metals that we have already discussed respond dramatically to this type of pretreatment. Reductions, in some cases, of up to 90 percent have been noted.

Again, may we stress that this type of pretreatment is designed for seepage flows and it must not be carried out in contact with iron sulphide bearing tails.

By now you may have realized that, although all seepage flows on any particular property should be combined before final discharge (see Rule #3), each individual flow can be treated by itself in any convenient depression. The overflow from each depression could then be directed to a common area where final treatment can take place.

Since acid mine drainage situations do generally not reach a peak until after the individual properties have been abandoned and since treatment must continue especially on abandoned properties, it is wise to avoid mechanical pumping wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

Rule #6

Make the maximum possible use of required water resources.

Acid mine drainage is more than just a problem of specific contaminants. It is a problem of volume. Most operations, for instance, would have no difficulty in adequately treating 8,000 gallons per day of typical acid mine drainage waste. But the treatment of 800,000 gallons per day would be a different matter. It is, perhaps, almost economically impossible under most circumstances.

The most effective way to minimize an overall acid mine drainage problem during the years of conventional mine-mill operations is to reduce the total volume of effluent that leaves the property. The most convenient way to reduce the total volume of effluent leaving the property is to set up the mine-mill complex on the basis of total or at least partial water recirculation.

We all realize, of course, that the re-use of water in most mine-mill operations is not as easy as it sounds. Flotation circuits, for instance, are noted for their extreme sensitivity. Even the simple re-use of underground (or open pit) mine water in the grinding circuit of a mill that employs normal froth flotation circuits can theoretically cause problems if the water contains significant quantities of organic materials such as oil. The occurrence of trace quantities of oily materials in underground mine water as a result of mining operations is not only possible but is probable. If oil is expected to be a problem at any operation, then all underground water should be pumped to a convenient depression on the surface near the mill. In the depression, oily materials will tend to separate and rise to the surface. Water, for re-use, should be taken from below the surface of this pond. If underground mine water is to be re-used in any mill that employs a froth flotation circuit, water soluble or emulsified oils should not be used underground. This type of oil will not easily respond to simple ponding.

With regard to underground mine water, the OWRC is recommending that all underground (or open pit) mine water be directed to the grinding circuit of the mill for re-use.

The recirculation of a tailings area decant involves even more than does the simple re-use of underground mine water. The tailings area decant can and often does contain residual quantities of the more persistent milling reagents. If the decant, therefore, is indiscriminately recirculated to the mill, the mill operator can lose partial control of the flotation process. The ensuing concentrate losses are serious not only from an economic standpoint but also from the standpoint that a portion of a non-renewable natural resource has been lost. On the other hand, if the discharge of contaminated decant wastes alters or destroys the life support properties of a watercourse or a watershed, the ultimate consequences may be even more far reaching.

Total recirculation systems are seldom what they imply. Seepage losses are usually great and as a result may cause a slow down the build-up of various dissolved solids in the recirculated liquid. In addition, most total recirculation systems require a decant bleed-off from time to time in order to control the dissolved solids content. This decant discharge must be chemically treated before it can be released to a watercourse.

The mining industry of Ontario is fortunate to have an extremely competent group of mining reagent suppliers. These people have demonstrated an interest not only in the efficiency of their products but also in the effects of their products on the mine worker and on the mine environment.

Close working cooperation is necessary between the various government agencies, the mine reagent suppliers and the mine operators to achieve a satisfactory solution to all the problems of wastewater recirculation. It is probable, for environmental reasons alone, that every mining operation in the Province of Ontario will be utilizing complete water recirculation systems by the end of this decade.

Rule #7

Do not needlessly contaminate unrequired water resources.

Under no circumstances should fresh water be permitted to gain access to a sulphide-bearing tailings area. All reasonable efforts should be made to divert streams and large springs around a tailings area or away from a tailings area. Once in a tailings area, fresh water tends to pick up quantities of acid-producing water soluble salts, etc. The result is that chemical treatment is required for water that is not needed in the mine-mill process. The real significance of this factor is generally acknowledged only after the property has been abandoned and profit-consuming waste treatment facilities must continue to be operated.

Excess water on a tailings area, particularly an abandoned tailings area, helps to maintain undesirable seepage flows and may heighten problems of instability of embankment structures.

Rule #8

Maintain the pH of all effluents at a level which will ensure the optimum precipitation of all metals including iron.

The overall solubility of Fe^{+2} and Fe^{+3} in mine water (f) is determined by many factors, none of which can be evaluated as an isolated variable. However, for both Fe^{+2} and Fe^{+3} the limiting solubility at any pH is the solubility satisfying the equations:

$$K_{\text{sol}} \text{ Fe (OH)}_2 = [\text{Fe}^{+2}] [\text{(OH)}^-]^2$$

and

$$K_{\text{sol}} \text{ Fe (OH)}_3 = [\text{Fe}^{+3}] [\text{(OH)}^-]^3$$

therefore:

Solubility of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ from K_{sol} at 25°C

$$K_{\text{sol}} \text{Fe}(\text{OH})_2 = 5.25 \times 10^{-14}$$

$$K_{\text{sol}} \text{Fe}(\text{OH})_3 = 1 \times 10^{-38} \quad (\text{also } 10^{-40} \text{ is reported})$$

<u>pH</u>	<u>Fe^{+2}, ppm</u>	<u>Fe^{+3}, ppm</u>
1		56,000
2		560
3		0.56
4		0.00056
5		
6	29,400	
7	294	
8	2.94	
9	0.0294	

Ferrous Iron

Equilibrium composition for the system $\text{Fe}^{+2} - \text{Fe}(\text{OH})_2$ at various pH values expressed as a fraction of the total Fe^{+2} present.

pH	5.0	6.0	6.5	7.0	7.5	8.0	9.0
Fe^{+2}	0.999	0.903	0.485	0.087	0.0094	0.00095	0.00001

Ferric Iron

Equilibrium composition for the system $\text{Fe}^{+3} - \text{Fe}(\text{OH})_3$ at various pH values expressed as a fraction of the total Fe^{+3} present.

pH	1.00	1.25	1.50	1.75	2.00	3.00
Fe^{+3}	0.8677	0.1947	0.0979	0.0213	0.0085	0.000008

The distribution of Fe^{+2} and $\text{Fe}(\text{OH})_2$ as a function of pH is graphically illustrated in Figure 1. Similarly, the distribution of Fe^{+3} and $\text{Fe}(\text{OH})_3$ as a function of pH is illustrated in Figure 2.

Figure 2 indicates that the ferric ion cannot exist, as such, in a solution having a pH much greater than 3.0. It must revert to a hydroxide-type form. Limited amounts of ferrous ion, however, can exist in solution at a pH of 8.0 (as indicated by figure 1). If a decant is maintained at a pH of 5.0 ferric iron in the overflow will be largely in the form of the relatively harmless hydroxide. However, it is possible that small quantities of ferrous ion will also exist in the overflow and hence leave the tailings area. If the ferrous ion is associated with the sulphate ion (as it usually is), then downstream oxidation will give rise to ferric sulphate that will hydrolyze to form ferric hydroxide and sulphuric acid. The probable result would then be a downstream pH depression. The downstream pH depression, of course, would create conditions whereby the ferrous ion could migrate even farther downstream and so on until a natural balance between the amount of acid being produced and the alkaline characteristics of the downstream environment was reached.

Obviously, if an operation is discharging an effluent at a pH of 7.5 and downstream pH problems are being encountered, not enough neutralizing agent is being added.

At a pH of 8.0 (necessary to meet the requirements of iron), many heavy metals do not precipitate to the extent that the resulting effluent can meet water quality standards. At a pH of 8.5, however, most problems are overcome. If undesirable quantities of specific metals (Zn, Ni, Mn, etc.) still remain in solution, the pH must be further increased.

Figures 1 and 2 indicate that at pH values less than 3.0 significant quantities of both ferrous and ferric iron can co-exist in solution and hence the acid mine drainage process becomes very efficient. Masses of hydroxides do not clog up oxidation sites or block solution passageways. Unfortunately, as the pH drops below 3.0, ideal conditions are set up for a bacterial attack on the sulphides. Once this attack is firmly established, the acid mine drainage process is practically irreversible.

Rule #9

Do not ignore the action of the wind on a tailings area.

Deflation (g) is by far the most important work of the wind and its significance can scarcely be over estimated. The lifting of material from a land surface is largely the work of eddies and irregularities of movement of the wind, including many conflicting cross-currents.

The most important are, of course, the eddies of whirlwinds and tornadoes but many minor currents, due in part at least to the irregularities of the surface, are active in lifting the dust and fine sand. The ordinary convection currents of the atmosphere carry this finer material up to great heights. The force, which moves the particle, is due to the direct impact of the wind, plus the friction along its surface. The force of the direct impact varies with the velocity of the wind, and for a given velocity with the cross-section of the particle in the plane perpendicular to the direction of the wind, as well as with the orientation of the particle and it is of course most efficient when a smooth plane is opposed to the wind. The resistance of the particle varies with its mass, i.e., its size and specific gravity and to some extent, its form. In general, the velocity of the wind necessary to carry a spherical particle of given specific gravity varies as the square of the radius and conversely, the radius of a particle which can be supported by wind varies as the square root of the velocity. It was found that a uniform upward current of air will keep suspended quartz grains, the size of which varied with the velocity, as follows:

<u>Velocity in meters per second</u>	<u>Diameter of quartz grain in mm</u>
0.50	0.04
1.00	0.08
2.00	0.16
3.00	0.25
4.30	0.35
5.00	0.41

<u>Velocity in meters per second</u>	<u>Diameter of quartz grain in mm</u>
6.00	0.49
7.00	0.57
8.00	0.65
9.00	0.73
10.00	0.81
11.00	0.89
12.00	0.97
13.00	1.05

From this, the formula $V = Kr$ was deduced, where K is a constant for the conditions of experiment and r the radius of the particle.

As a result of numerous measurements, the conclusion reached was that the average largest size of quartz particles that can be sustained in the air by ordinary strong winds is about 0.1 mm in diameter but the largest particle that can be transported (not held in suspension) is nearer 2 mm in diameter. This represents the limit of ordinary deflation.

The following table gives the approximate size of quartz sand grains moved by varying wind velocities.

<u>Strength of wind in meters per second</u>	<u>Maximum diameter of sand grains in mm</u>
4.5 - 6.7	0.25
6.7 - 8.4	0.5
9.8 - 11.4	1.0
11.4 - 13.0	1.5

These results are only approximate.

Problems due to wind blown tailings have been encountered at nearly every mining camp in Ontario.

Take, for example, the situation at Mine X. A large unbroken expanse (300 acres) of dry sulphidic tailings was

exposed to the action of the wind. During the summer of 1968, it became apparent that swampy areas and "pot-hole" lakes located in the vicinity of the tailings area were contaminated although no normal link to the tailings area could be established. The colour changes in these waters were observed to be identical to the colour changes taking place in waters that were directly exposed to the tailings and, therefore, the possibility of the aerial transport of finely divided tailings from the tailings area to the waters in question could not be ignored.

The first step in our preliminary investigation of the airborne tailings was to secure a sample of tailings that we knew had already undergone some degree of aerial transport. Since deposits of wind-blown sand were easily recognizable and readily available in and around the tailings area, we selected this as our sample source.

The following are the actual average analytical results of the samples in question:

Total iron as Fe	-	2.05%
Calcium as Ca	-	0.013%
Sodium as Na	-	0.006%
Potassium as K	-	0.316%
Phosphorus as P	-	0.033%
Aluminum as Al	-	0.68%
Titanium as Ti	-	0.046%

The above values were obtained by leaching the sample and therefore represent the material available to the natural processes of chemical decomposition and reaction. The iron content is, quite unexpectedly, very high. The bulk of the sample was composed of silicon dioxide (an "inert" material in this context).

A sieve analysis was also run on the wind-blown samples and serves, at least, to identify the size fractions that can be moved by the wind at this mining property:

	Retained by No. 10 mesh -	0.021%
Passed by No. 10, Retained by No. 25 mesh -		0.029%
Passed by No. 25, Retained by No. 45 mesh -		1.47%
Passed by No. 45, Retained by No.100 mesh -		85.3%
Passed by No.100, Retained by No.200 mesh -		11.7%
Passed by No.200 mesh		1.44%

Assuming that the samples were representative, it is immediately apparent that particles that will not pass through a 45 mesh screen (U.S. Standard Sieve) are generally too large to be subject to aerial transportation. On the other hand, particles that are small enough to pass through a 45 mesh screen will undergo active aerial transportation should the required conditions present themselves.

It is necessary to point out that the above sieve analysis reflects the characteristics of the wind-blown deposits after they have undergone some degree of aerial transport. In other words, we have to assume that most of the fine (-200 mesh) material was removed by wind action from the deposits before we sampled them.

Analysis of the residual -200 mesh fraction revealed that it contained 15.2 percent iron as Fe. In other words, the fine dust that is blown from the tailings area and that eventually settles on the land and in the stagnant lakes and streams in the immediate area could possibly have contained up to 30 percent sulphides.

Many common methods, including revegetation and the use of artificial windbreaks, are known by which wind erosion can be controlled. As such, no further discussion is required.

Rule #10

Revegetate abandoned tailings areas and the downstream slopes of all tailings dams whenever and wherever possible.

A well-developed continuous cover of vegetation on abandoned tailings areas and on the downstream slopes of all dams will ensure, to some degree, regulation of the effects

of natural precipitation. Runoff, for all intents and purposes, will be eliminated. The volume of some seepage flows will be significantly reduced. The effects of the wind will be negligible. The area will blend into the surrounding landscape.

Recent legislation of the Ontario Department of Mines and Northern Affairs requires the "rehabilitation of tailings disposal and plant areas". Since it must be done, it may as well be done in such a manner that the problems of acid mine drainage are lessened.

In this paper, we have outlined the basic factors that are involved in the formation of acid mine drainage in the Province of Ontario. The chemical reactions responsible for acid mine drainage have been confirmed not only in Ontario but in other Provinces and in other countries.

It must be recognized that, while the basic problem of acid mine drainage is a common one, the extent of the problem and the factors causing the problem vary from property to property. For this reason, the solution to any particular problem of acid mine drainage depends largely on local circumstances. The geography of the property and the composition of the ore and country rocks are extremely important.

The rules that we have presented should be considered in special detail before the construction of a mine, a mill or a tailings area actually commences. When dealing with an existing problem of acid mine drainage, these rules should be applied whenever and wherever possible.

We are confident that the general implementation of these rules by the mining industry of Ontario would result in the virtual elimination within the Province of the problem known as 'acid mine drainage'.

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ASPECTS OF ACID MINE DRAINAGE IN

SULPHIDE MINING AREAS

by

John R. Hawley

(An article published by "The Northern Miner", Spring 1971)

In coal mining areas, acid mine drainage is an old and well-known problem. In sulphide mining areas, the problem is new and was somewhat unexpected.

Pyrite, a common disulphide of iron, was found to be the cause (or source if you wish) of acid mine drainage in coal mining areas. Pyrite, in a finely divided state and in direct or indirect contact with our atmosphere, undergoes a process of chemical decomposition. Many of the products of decomposition are water soluble and have an ability to affect stream chemistry and ecology.

The basic reactions that describe the chemistry of an acid mine drainage situation are well-known and are detailed here simply as a review:

Reaction #1 - (Sulphide to Sulphate)

When pyritic material is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition.

- (a) Assuming that the reaction takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:



- (b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate

in equal parts results:



In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 - (Oxidation of Iron-Ferrous to Ferric)

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:



Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (T. ferrooxidans) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 - (Precipitation of Iron)

The ferric iron associated with the sulphate ion commonly combines with the hydroxyl $(\text{OH})^-$ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:



Important Note

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion

"backtriggers" the oxidation of further amounts of pyritic materials to the sulphate form thereby accelerating the acid-forming process:



In Ontario, when acid mine drainage type effluents were evident, the specific companies involved worked sulphide or sulphide-associated ores. The related ore bodies contained quantities of iron sulphide (in various mineralogical forms) and the milling circuits, serving these operations, were such that the iron sulphides were rejected to the tailings areas as waste. Once in the tailings areas and after varying periods of time, the iron sulphides began to break down chemically. Acid mine drainage was the result.

When present, iron sulphide occurs in three principal forms in most tailings areas:

- (1) pyrite
- (2) marcasite
- (3) pyrrhotite

Pyrite is an isometric form of ferrous disulphide. Marcasite is also ferrous disulphide but is orthorhombic in nature. Pyrrhotite is a hexagonal form of ferrous sulphide that contains a slight excess of sulphur.

The rates of reaction of pyrite, marcasite and pyrrhotite under typical acid mine drainage circumstances are significantly different. Generally, however, most tailings areas contain intimate mixtures of two or more iron sulphide species. In addition, severe acid mine drainage problems are known to occur in Ontario where the most reactive species (marcasite and pyrrhotite) are, relatively speaking, absent.

Tailings areas that are well-known as acid producers within the Province of Ontario have been examined in detail. The iron sulphide content of the areas studied varied from a minimum of 2.5 percent to a maximum of 72 percent. Many properties with sulphide contents within this range are known.

The iron sulphides, of course, are not the only sulphides that find their way into the tailings areas. Mill recoveries are seldom greater than 97 percent and, as such, limited quantities of ore materials also become an integral part of a tailings mass. The ore materials are generally sulphides themselves (chalcopyrite, sphalerite, etc.) and, therefore, enter into oxidation reactions that, in a simple sense, tend to resemble the iron sulphide oxidation reactions that have already been described.

When the correct conditions are presented, sulphide minerals in a tailings mass will oxidize to the corresponding metal ions plus the sulphate ion. Iron, copper, cobalt, manganese, zinc and nickel, for instance, all form soluble salts (usually sulphates) under acid mine drainage conditions and are, therefore, commonly detected in the flows from affected areas. Lead, on the other hand, forms a relatively insoluble sulphate (known as the mineral anglesite in geology texts) and is, therefore, only rarely detected in concentrations greater than 1 part per million under similar circumstances.

A tailings area of the type we are discussing can be regarded as nothing more than a highly fractured sulphide 'ore body'. The enormous secondary surface area of the 'ore body' has been created mechanically as a result of crushing and grinding in the mill. Oxygen-carrying water has ultimate access to virtually every particle in the mass. It is only logical to suspect therefore that a tailings area that contains quantities of iron sulphide will (unless the gangue in the original ore has sufficient residual neutralizing capacity and this is generally not the case) produce large quantities of water-soluble acid-producing salts.

Acid mine drainage is a waste that is characterized by:

- (1) a relatively low pH;
- (2) a relatively high sulphate content;
- (3) a relatively high iron content;
- (4) the presence of an abnormal concentration of many metals such as manganese, nickel, cobalt, zinc and copper.

- (5) a tendency to change colour on standing (clear and colourless to yellow to deep amber red).

Many metals have been detected in undesirable concentrations in acid mine drainage type effluents and treatment for the removal of these metals must be provided. The absolute extent to which these metals affect the aquatic environment is currently being determined.

The main sources of the metals in the water leaving a pyritic tailings area are the iron sulphides themselves and not the associated ore sulphides. Several metals (e.g. nickel and cobalt) can substitute for iron in the iron sulphide lattice. Hence nickelian and cobaltian varieties of pyrite are known. When the pyrite breaks down in the above cases, nickel and cobalt go into solution. Spectroscopic traces of vanadium, molybdenum, chromium, tungsten and thallium have all been reported in pyrite. Copper is also commonly recorded but is presumably due to microscopic impurities (inclusions, etc.) in the pyrite mass itself.

The ore sulphides do break down slowly and are the major source of many of the less well-known metal species that go into solution. However, the total contribution of the ore sulphides to the severity of the overall acid mine drainage situation is, at the present time, not well known.

If sufficient care is taken during the years of conventional mine-mill operations, the inherent alkalinity of most flotation circuits plus perhaps minor lime additions should control any tendency towards an acid mine drainage situation where the main decant is concerned. However, during the same period, that is, the operational life of the mine-mill complex, there is a very good chance that the underflow (seepage) from the tailings area will gradually become highly acid in nature and will, therefore, require extensive chemical treatment if environmental standards are to be maintained. In the Province of Ontario, the primary cause of downstream acid mine drainage problems relating to a specific operation has been found to be the untreated seepage discharges from active tailings areas plus uncontrolled runoff and seepage from abandoned areas.

Acid mine drainage is cumulative. Abandoned properties will continue to produce 'acid' for decades. As the number of

abandoned sulphide operations increases, the acid load that our environment must absorb also increases. Considering that, at the present time, almost fifty square miles of the Province of Ontario are covered by active and abandoned tailings areas and considering that a very healthy percentage of these areas are pyritic in nature, we can easily see that the problem facing the mining industry is significant in terms of environmental control.

While the basic problem of acid mine drainage is very common, the extent of the problem and the factors causing the problem vary from property to property. For this reason, the solution to any particular problem of acid mine drainage depends largely on local circumstances. Of extreme importance is the composition of the ore, the composition of the country rock and the geography of the property.

"ASPECTS OF THE PROBLEM OF ACID MINE DRAINAGE
IN THE PROVINCE OF ONTARIO"

by

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A Paper Presented at the
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Introduction

The rapid industrial development and utilization of natural resources in the Province of Ontario has presented many problems concerning our water environment. A tremendous upsurge in mining exploration and development in the past two decades plus uncorrected situations having origins in the mining activities of the early part of this century have resulted in serious deterioration of the quality of the water in many watersheds of the north where mining operations are carried out.

Acid mine drainage is a major environmental problem in Ontario's hardrock mining districts. Curiously enough, most specific acid mine drainage problems are not the result of indiscriminate hardrock mining activity but, instead, form a condition of it. The problem may occur whenever an orebody containing iron sulphides is exposed to the atmosphere.

The problem of acid mine drainage is not unique to Ontario. It is well known in other Provinces, the United States, Europe and Japan. In fact, acid mine drainage probably occurs on a worldwide basis.

The problem of acid mine drainage in Ontario begins when a mine-mill operation, during the processes of ore comminution and beneficiation, discards, as waste, the various iron sulphide minerals that occur naturally in the ore. These iron sulphides, finely divided as a result of milling operations, are, along with other gangue (non-valuable) materials discharged as a slurry to a natural or man-made settling basin that is commonly referred to as a tailings area. Here, the slurry undergoes a natural solid-liquid separation and, under ideal conditions, the solid particles, including the iron sulphide minerals, are retained within the confines of the tailings area. The clarified liquid escapes the area via a structure called the decant and as seepage through the bases of permeable dams.

Once in a tailings area and after a varying period of time, the iron sulphide minerals react to form water soluble salts which, when discharged in the effluent from a tailings area, can affect stream chemistry and stream ecology.

The Chemistry of Acid Mine Drainage

This paper deals exclusively with the type of acid mine drainage problem that results when naturally occurring inorganic sulphides undergo spontaneous decomposition. The basic reactions that describe the chemistry of this type of situation are as follows:

Reaction #1 (Sulphide to Sulphate)

When natural sulphuritic material in the form of a sulphide (and usually in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition:

(a) Assuming that the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:



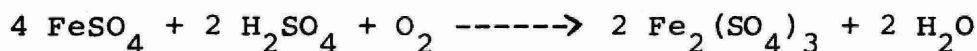
(b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:



In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 (Oxidation of Iron (Ferrous to Ferric))

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:

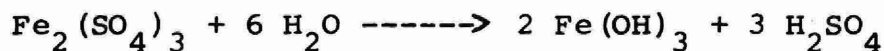


Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (*T. ferrooxidans*) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 (Precipitation of Iron)

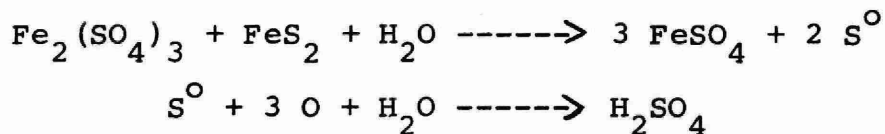
The ferric iron associated with the sulphate ion commonly combines with the hydroxyl (OH)⁻ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:



IMPORTANT NOTE

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-

forming process:



Sources and Characteristics of Acid Mine Drainage

At the present time, approximately fifty square miles of the Province of Ontario are covered by active and abandoned tailings areas. Many of these areas are pyritic in nature. The significance of this is that acid mine drainage is a cumulative problem because abandoned properties continue to produce 'acid' for decades. Therefore, as the number of abandoned sulphide operations increases, the acid load to the environment also increases.

In the past, two types of sulphide deposits have not been commercially recoverable in Ontario. One was the relatively low grade, large volume type of deposit and the other was the type of deposit that was characterized by complex fine-grained sulphide assemblages. In general, both of these types of deposits are now being successfully worked. The low grade, large volume type of deposit generates large volumes of tailings that may or may not contain significant quantities of iron sulphides. The complex sulphide-assemblage type of deposit is frequently associated with large quantities of the iron sulphide minerals which, as stated before, are rejected to tails as wastes. Many individual pyritic tailings areas in the Province cover hundreds of acres and many new large ones are expected. One such tailings area in the Province will ultimately cover nearly four square miles and will have an inherent iron sulphide content in excess of 30 percent.

Tailings areas that are well known as acid producers in the Province of Ontario have iron sulphide contents ranging from 2.5 percent to 72 percent. It is suspected that acid mine drainage conditions will occur even when the iron sulphide content of a tailings mass is less than 2.5 percent.

Complex sulphide assemblages frequently require very fine grinding in order to liberate individual sulphide species. The individual species are recovered as separate concentrates by a process called differential

flotation. Unfortunately, the iron sulphide minerals in the ore must also suffer the fine grinding procedure. As the grind becomes finer, the relative surface area of each sulphide particle increases. As the relative surface area of each sulphide particle increases, the probability of an acid mine drainage situation increases. Two years ago, a mill grind of 65 percent minus 200 mesh was common. Today, grinds finer than 300 mesh are becoming common.

The iron sulphides, pyrite, pyrrhotite and marcasite are not the only sulphides that are discharged to a tailings area. There are over 125 naturally occurring inorganic sulphides and sulphosalts and many of these are well known 'ore' sulphides. Since mill efficiencies are seldom greater than 97 percent, limited quantities of these sulphides also gain access to a tailings area. The 'ore' sulphides are subject to chemical attack especially under the extreme conditions that are created by the oxidation of the iron sulphides.

Some metals, cobalt and nickel for example, can substitute for iron in the iron sulphide lattice. When the iron sulphide lattice breaks down, these metals also go into solution if the sulphide is in an aqueous environment.

Acid conditions are frequently generated in underground mining environments where oxygen-carrying water is permitted to come into contact with sulphide-bearing rock masses. This water must be removed from the mine and its disposal is a problem.

Typical acid mine drainage flows are characterized by a low pH, a high iron concentration, a high sulphate concentration and an abnormal heavy metals concentration. Manganese, copper, cobalt, zinc and nickel are all commonly found in acid mine drainage flows. The list of the possible anions and cations that can occur in an acid mine drainage type effluent is almost endless.

Soluble iron compounds, which are an integral part of most acid mine drainage flows, tend to oxidize over a period of time. The resulting complexes or finely-divided precipitates are various shades of yellow or red in colour. Amber stagnant pools of this type of waste and yellow-tinted seepage flows typify a mining camp

that is, or has been, subject to acid mine drainage.

The development of an acid mine drainage situation at a mining property is probable if:

- (a) the ore (including country rock) being milled contains iron sulphide minerals; and
- (b) the ore (including country rock) does not naturally contain enough carbonate or similar material to effectively neutralize all the 'acid' that will result from the decomposition of the iron sulphides.

The probability of an acid mine drainage situation increases:

- (a) with an increase in fineness of grind in a mill circuit. As the grind becomes finer, the total available surface area for reaction increases.
- (b) with an increase in the number of permeable dams on the property or with an increase in the length of existing permeable dams on the property. Seepage flows through the dams act as the transport medium for the soluble reaction products of sulphide decomposition. If the soluble reaction products are not removed, connecting pore spaces in the tailings mass become clogged with these substances and the acid mine drainage mechanisms are forced to slow down because of a lack of available oxygen, water and soluble ferric iron.
- (c) with the return of untreated seepage from the bases of dams to the main tailings area. In acid mine drainage situations, untreated seepage contains quantities of dissolved ferric iron. This ferric iron can cause the oxidation of further amounts of iron sulphide should it come into contact with iron sulphide.

Chemical Treatment of Acid Mine Drainage

The treatment of acid mine drainage at the present time involves some form of neutralization. Neutralization is necessary to control pH and to precipitate soluble metallic species. In some instances, neutralization to a minimum pH of 8.5 is sufficient. In other instances, a minimum pH of 8.5 will still leave a few metals in solution. Accordingly, the pH must be

increased until, if technically feasible, total precipitation is achieved. Where the pH is increased to a very high level (over 10) to achieve total precipitation of the metals, adjustments will be required to reduce the pH to normal levels prior to discharge to a water-course.

Generally, five common neutralizing agents are available for use:

- (1) ammonia
- (2) sodium hydroxide
- (3) sodium carbonate
- (4) limestone
- (5) lime

Because of its toxicity and nutrient properties, ammonia should never be used as an effluent neutralizing agent. Similarly, the use of ammonia and ammonium based compounds in a mill circuit should be avoided.

Sodium hydroxide and sodium carbonate are both acceptable as neutralizing agents but, because of their costs, do not find wide use. There is, however, an ecological advantage in using sodium carbonate as it will tend to offset any inorganic carbon deficiency in water that may result from discharges of the acid mine drainage type.

Lime and limestone are the most commonly used neutralizing agents. Lime finds the greatest use and, from a chemical standpoint, is the preferred reagent. Lime is generally available, has a high basicity and the cost, while high, is less than all other neutralizing agents with the exception of limestone. Lime is a very reactive material with the neutralizing reaction going to completion within one hour. High pH's can be obtained and maintained with lime. In Ontario, where the removal of inherent heavy metal concentrations is required, this capability is very important.

The attractiveness of limestone as a neutralizing agent centres primarily on its low initial cost per unit weight and the fact that it presents almost no problems with regard to handling and storage. Its disadvantages, however, are numerous. The limestone

neutralization reaction is slow and often requires from 24 to 48 hours to go to completion. The long detention time that is generally required after limestone addition to an acid effluent becomes significant when the land upon which the retention facilities are built is expensive or when numerous impoundment structures are required. Aeration may reduce the retention time to one comparable to lime. Neutralization with limestone tends to become inefficient above pH values of 4.0. pH's above 7.0 are obtained and maintained with some difficulty. Total utilization of the potential alkalinity of limestone can drop to approximately 31 percent. In contrast, the utilization efficiency of lime is generally in excess of 97 percent. During the neutralization process, the limestone particles become coated with insoluble reaction products. If this coating is not continuously removed, the reaction is retarded. In any case, the limestone reaction seldom goes to completion and the resulting limestone sludge contains a residual alkalinity that is of questionable value. Limestone, under most circumstances, exhibits an inability to effect complete control of dissolved ferrous iron whereas lime handles this material with relative ease. In Ontario, where acid seepage flows frequently contain considerable concentrations of dissolved ferrous iron, this is an important factor. One dubious advantage of the limestone reaction is that it is not very sensitive quantitatively and therefore the accuracy with which limestone is fed into an effluent stream need not be controlled to the same degree as that required by lime.

Fixed beds of limestone are not recommended for neutralization of final effluents.

When acid mine drainage conditions prevail, iron is the principal metal found in solution. Depending on many factors, the iron will be either in the suspended or dissolved form and in the ferrous (Fe^{++}) or the ferric (Fe^{+++}) state. In the pH range below 3.0, most of the ferrous and ferric iron will be in solution. In the pH range 3.0 to 8.0, the ferric iron should all be in a precipitate form and, while much of the ferrous iron will also be in a precipitate form, a significant portion of the ferrous iron will also be in solution. In the pH range above 8.0, essentially all iron species are insoluble and hence precipitate. In acid mine drainage circumstances, ferrous and ferric

iron are generally associated with the sulphate radical. Ferric sulphate hydrolyzes in an aqueous environment to form an insoluble hydroxide plus sulphuric acid. The acid released can cause a pH depression. Ferrous iron in a stream will oxidize to the ferric form and then hydrolyze to form the hydroxide and sulphuric acid. Since ferrous iron exhibits a greater stability in acid and somewhat alkaline environments than does ferric iron, the ferrous ion has the potential ability to migrate much farther from a tailings area than does the ferric ion. However, as the distance between the ferrous ion and the tailings area increases, conditions for the survival of the species deteriorates and, ultimately, oxidation and hydrolysis takes place.

Several chemical agents which are indigenous to mine drainage waters have been cited in the literature, in various circumstances, as displaying catalytic properties in the oxidation of ferrous iron. These include inorganic ligands, such as sulphate, which coordinate with iron (II) and iron (III); soluble metal ions such as copper (II), manganese (II), and aluminum (III); suspended material with large surface areas and high adsorptive capacities such as clay particles; and materials which accelerate the decomposition of peroxides in the presence of iron (II) such as charcoal.

Microbiological Aspects of Acid Mine Drainage

A topic that is frequently associated with the subject of acid mine drainage is microbiological leaching of sulphide minerals. Microbiological leaching involves the oxidation of the sulphide portion of various metallic sulphides with the subsequent release of the metal values into solution. Three names have been given to bacteria capable of oxidizing sulphide minerals:

- (1) Thiobacillus ferrooxidans;
- (2) Ferrobacillus ferrooxidans; and
- (3) Thiobacillus sulfooxidans.

However, it has been shown that there is no justification for separating the bacteria into different genera and species and, as such, the name T. ferrooxidans has been suggested for the group.

Like many bacteria, T. ferrooxidans is ubiquitous, and its activities are manifested in leach-

ing wherever a sulphide substrate, oxygen, carbon dioxide, water, certain essential nutrients and the correct pH make up a suitable environment.

T. ferrooxidans belongs to a somewhat select group of bacteria which are rather independent in temperament, and which probably existed on this earth long before those other microbial forms which are interdependent for many of their foods and conditions of life. In contrast to most bacteria, *T. ferrooxidans* uses atmospheric carbon dioxide as its sole source of the carbon necessary for the generation of cellular material. Rather than utilizing organic matter such as fats, carbohydrates or proteins as a source of energy, this organism cannot even tolerate their presence, and obtains its energy solely by the oxidation of inorganic materials such as ferrous iron or sulphur in the form of elemental sulphur or as metallic sulphides.

T. ferrooxidans has adapted itself to live and grow in the strongly acidic environment (pH 1.5 - 3.0) which results from the oxidation of sulphides, and in the presence of many heavy metals which are released into solution from minerals concurrent with the oxidation of ferrous iron and sulphides. In order for *T. ferrooxidans* to function in the biological leaching of sulphides, the pH must be below 4 and preferably below 3. Apparently, the organism can oxidize sulphur at pH's as high as 5, but it will only occasionally oxidize sulphide at pH's above 3.5, and never above 4.0.

In attacking the sulphide moiety in crystalline or amorphous substances, the bacteria convert the sulphide to sulphate and, with the disruption of the solid matrix, the metal ions go into solution. These metals remain in solution as water-soluble sulphates initially, although iron may be subsequently precipitated as the insoluble hydroxide or basic sulphate. The hydrolysis of the ferric sulphate produces sulphuric acid along with either the ferric hydroxide or basic ferric sulphate. The sulphuric acid modifies the pH in the micro-environment immediately surrounding the bacteria. If there is no external disruption, the pH frequently tends to stabilize near pH 2 due to the resolubilization of ferric hydroxide. If there is excess pyrite or pyrrhotite present, it will go lower; pH values as low as 0.9 having been attained. pH values below 1.2 have a def-

inite detrimental effect on the bacteria, interfering with their activity and resulting in the production of elongated cells.

Although T. ferrooxidans survives in conditions that are highly toxic to most other forms of life, it still must have oxygen to live. Every pound of sulphur (either as native sulphur or as sulphide) requires two pounds of oxygen for complete conversion to sulphate. Similarly, the bacteria require 0.14 pounds of oxygen for every pound of iron converted from the ferrous to the ferric form.

Phosphate and ammonia appear to be the most critical nutrients with regard to the nutrient requirement of T. ferrooxidans.

Temperature is another factor which can influence biological leaching. The optimum temperature for biological leaching has been found to be 35°C . The bacteria are inhibited at temperatures of 40°C and above. When no other factors have become rate controlling, the rate of leaching decreases as the temperature decreases; as yet, however, no minimum temperature has been established. Leaching is known to occur slowly at 3°C to 6°C .

Substrates Oxidized by Thiobacillus Ferrooxidans

<u>Substrate</u>	<u>End Product</u>
Ferrous Iron Fe^{++}	Fe^{+++}
Trithionate $\text{S}_3\text{O}_6^{=}$	$\text{SO}_4^{=}$
Tetrathionate $\text{S}_4\text{O}_6^{=}$	$\text{SO}_4^{=}$
Thiosulphate $\text{S}_2\text{O}_3^{=}$	$\text{SO}_4^{=}$
Sulphur S^0	$\text{SO}_4^{=}$
Sulphide $\text{S}^{=}$	$\text{SO}_4^{=}$

Metallic Sulphides Known to be Oxidized by Thiobacillus Ferrooxidans

Arsenopyrite - $\text{Fe}_2\text{As}_2\text{S}_2$	Millerite - NiS
Bornite - Cu_5FeS_4	Molybdenite - MoS_2
Bravoite - $(\text{Ni}, \text{Fe})\text{S}_2$	Orpiment - As_2S_3
Chalcocite - Cu_2S	Pyrite - FeS_2
Chalcopyrite - CuFeS_2	Pyrrhotite - Fe_7S_8
Cobaltite - CoAsS	Sphalerite - ZnS
Covellite - CuS	Stannite - $\text{Cu}_2\text{FeSnS}_4$
Enargite - $\text{Cu}_3(\text{As}, \text{Sb})\text{S}_4$	Tetrahedrite - $\text{Cu}_8\text{Sb}_2\text{S}_7$
Marcasite - FeS_2	Violarite - $(\text{Ni}, \text{Fe})_3\text{S}_4$
Marmatite - $(\text{Zn}, \text{Fe})\text{S}$	

The Reaction of Non-Sulphide Minerals Under Acid Mine Drainage Conditions

The decomposition of sulphides in a tailings area frequently creates chemical conditions that adversely affect the stability of many of the non-sulphide mineral species that are present. Although these non-sulphide minerals are, in general, characterized by their relative stability in a natural environment, they do break down very slowly and release anions and cations that help to make up natural background concentrations. In a tailings basin, the enormous overall surface area of the tailings mass itself is such that the slow breakdown of the various non-sulphide minerals becomes significant since the soluble reaction products frequently end up in a concentrated form in the seepage or decant overflow from the area. A few grams of tailings taken from almost any disposal area will contain at least traces of most of the elements known to man. It is for this reason that strict attention must be paid to the type and reactivity of all minerals that occur in or are associated with an orebody. As an example, consider the rocks known as granite and diabase. Both occur commonly in and around ore bodies. Granite is essentially composed of feldspar

and quartz. Minor constituents may include muscovite, biotite, hornblende and, rarely, pyroxene. Diabase is essentially a mixture of feldspar and pyroxene. Table I, presented at the end of this paper, indicates the relative amounts of the various elements that could be released if total decomposition of granite and diabase took place.

If complete treatment is not provided, an exposed tailings area, particularly if it is subject to an acid mine drainage situation, will permit the escape of many unwanted materials into our natural aqueous environment.

Revegetation

The revegetation of abandoned mine tailings in the Province of Ontario is now mandatory under the provisions of The Mining Act.

The presence of a well-developed cover of vegetation reduces the effects of acid mine drainage by regulating the effect of natural precipitation and thereby reducing the volume of acid seepage flows. However, a vegetative cover does not completely eliminate seepage flows and, as a result, some form of chemical treatment of waste flows is generally still required.

The revegetation of tailings areas that contain quantities of the iron sulphide minerals is difficult and expensive. The main problem is the acid condition that is generated by the slow decomposition of the sulphide minerals. The 'acid' that is produced must be neutralized before any seeding of the area is attempted. In addition, a large reserve of residual alkalinity must be provided so that 'alkalinity' is available on a continuous basis. The iron sulphides spontaneously produce acid and, if this is not neutralized as it is formed, a 'kill' of any established vegetation could take place. However, it is probable that, once a cover of vegetation has been established, naturally introduced acid tolerant species of vegetation will take over.

The initial neutralization of the upper few inches of an acid tailings area prior to seeding can be accomplished with powdered lime or finely-divided limestone or a mixture of both. The residual alkalinity

should be attained and maintained with a graded limestone product.

Limestone tends to be quite expensive in the mining districts of Ontario simply because the mining camps are frequently to be found considerable distances from the limestone producing centres in southern Ontario.

It should be emphasized that the limestone required for maintaining alkalinity in the upper layers of a pyritic tailings area need not be pure. Quite often the limestone can be found in sedimentary strata, sedimentary outliers, or metamorphic equivalents of carbonate sediments within a reasonable trucking distance of the mining operations. Gravel deposits that have been derived by glaciation from the aforementioned often contain significant quantities of carbonate pebbles. Pit-run or screened gravel is much cheaper than crushed limestone.

Water Recirculation

When mining activities began in the Province over one hundred years ago, there was little apparent need for strict water conservation. Today, the awareness and demands of a rapidly increasing population have changed the picture dramatically. Even the most remote mining operation is now subject to stringent environmental controls.

Wastewater re-use is a very effective way to lessen the impact of a mining operation on its immediate environment. By reducing the total volume of waste discharged from any particular operation, water recycle permits several mining companies to exist with some degree of environmental compatibility on a single lake, single watercourse, or single watershed. This sharing of a restricted area is the rule rather than the exception in the mining industry.

The most effective way to minimize an overall acid mine drainage problem during the years of conventional mine-mill operations is to reduce the total volume of effluent that leaves the property. The most convenient way to reduce the total volume of effluent leaving the property is to set up the mine-mill complex on the basis of total or at least partial water recircula-

tion.

Total recirculation in many sections of the mining industry is not easy to attain. Flotation circuits, for instance, are noted for their sensitivity. Even the simple re-use of underground (or open pit) mine water in the grinding bay of a mill that employs normal froth flotation circuits can theoretically cause problems if the water contains significant quantities of organic materials such as oil. The occurrence of trace quantities of oily materials in underground mine water as a result of mining operations is not only possible but is probable. The recirculation of a tailings area decant involves even more. The tailings area decant can and often does contain residual quantities of the more persistent milling reagents. If the decant is indiscriminantly recirculated to the mill, the mill operator can lose partial control of the flotation process with the result that valuable concentrate is lost. Similarly, abnormal quantities of soluble and suspended materials that are reintroduced into a mine-mill circuit have a potential ability to adversely affect basic operations such as ion exchange, thickening, filtration, precipitation and pH control. When all of this is added to the fact that most underground mines naturally "make" more water than can be used in underground mining operations and the fact that natural precipitation on a tailings area frequently creates a significant oversupply of water as far as recirculation from a tailings area decant to a mill is concerned, it becomes obvious that total recycle is often impossible to achieve. However, partial recycle is possible in nearly every case.

All new mine-mill complexes coming into production in the Province of Ontario are currently being requested to set up their mine-mill operations on the basis of maximum possible water re-use. In existing problem areas, mining operations are also being requested to effect maximum possible water re-use.

Summary

Acid mine drainage is one of the greatest single environmental problems facing the sulphide mining industry in Ontario today. Quick and intelligent action is required. A parallel can be drawn to the mining districts of the eastern United States where neglect of the

problem of acid mine drainage has led to the impairment of over 10,000 miles of previously unaffected water-courses.

The industrial wastes program in Ontario contains the ingredients necessary to adequately control the major aspects of any acid mine drainage problem. However, complete control will be won only through the concerted efforts of government agencies coupled with the absolute cooperation of the industries involved.

TABLE I

The Average Amounts of the Elements in Crustal Rocks
in Parts Per Million

(omitting the rare gases and the short-lived
radioactive elements)

<u>Atomic Number</u>	<u>Element</u>	<u>Crustal Average</u>	<u>Granite</u>	<u>Diabase</u>
1	H	1,400	400	600
3	Li	20	24	12
4	Be	2.8	3	0.8
5	B	10	2	17
6	C	200	200	100
7	N	20	8	14
8	O	466,000	485,000	449,000
9	F	625	700	250
11	Na	28,300	24,600	15,400
12	Mg	20,900	2,400	39,900
13	Al	81,300	74,300	78,600
14	Si	277,200	339,600	246,100
15	P	1,050	390	650
16	S	260	175	135
17	Cl	130	50	
19	K	25,900	45,100	5,300
20	Ca	36,300	9,900	78,300
21	Sc	22	3	34
22	Ti	4,400	1,500	6,400
23	V	135	16	240
24	Cr	100	22	120
25	Mn	950	230	1,320
26	Fe	50,000	13,700	77,600
27	Co	25	2.4	50

<u>Atomic Number</u>	<u>Element</u>	<u>Crustal Average</u>	<u>Granite</u>	<u>Diabase</u>
28	Ni	75	2	78
29	Cu	55	13	110
30	Zn	70	45	82
31	Ga	15	18	16
32	Ge	1.5	1.0	1.6
33	As	1.8	0.8	2.2
34	Se	0.05		
35	Br	2.5	0.5	0.5
37	Rb	90	220	22
38	Sr	375	250	180
39	Y	33	13	25
40	Zr	165	210	100
41	Nb	20	20	10
42	Mo	1.5	7	0.05
44	Ru	0.01		
45	Rh	0.005		
46	Pd	0.01	0.01	0.02
47	Ag	0.07	0.04	0.06
48	Cd	0.2	0.06	0.3
49	In	0.1	0.03	0.08
50	Sn	2	4	3
51	Sb	0.2	0.4	1.1
52	Te	0.01		
53	I	0.5		
55	Cs	3	1.5	1.1
56	Ba	425	1,220	180
57	La	30	120	30
58	Ce	60	230	30
59	Pr	8.2	20	2

<u>Atomic Number</u>	<u>Element</u>	<u>Crustal Average</u>	<u>Granite</u>	<u>Diabase</u>
60	Nd	28	55	15
62	Sm	6.0	11	5
63	Eu	1.2	1.0	1.1
64	Gd	5.4	5	4
65	Tb	0.9	1.1	0.6
66	Dy	3.0	2	4
67	Ho	1.2	0.5	1.3
68	Er	2.8	2	3
69	Tm	0.5	0.2	0.3
70	Yb	3.4	1	3
71	Lu	0.5	0.1	0.3
72	Hf	3	5.2	1.5
73	Ta	2	1.6	0.7
74	W	1.5	0.4	0.45
75	Re	0.001	0.0006	0.0004
76	Os	0.005	0.0001	0.0004
77	Ir	0.001	0.006	
78	Pt	0.01	0.008	0.009
79	Au	0.004	0.002	0.005
80	Hg	0.08	0.2	0.2
81	Tl	0.5	1.3	0.13
82	Pb	13	49	8
83	Bi	0.2	0.1	0.2
90	Th	7.2	52	2.4
92	U	1.8	3.7	0.52

RECOMMENDED REFERENCES

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